

June 6, 1950

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2,510,071

VITREOUS ENAMELING OF FERROUS METAL

Filed Aug. 9, 1945

2 Sheets-Sheet 1

Fig. 1

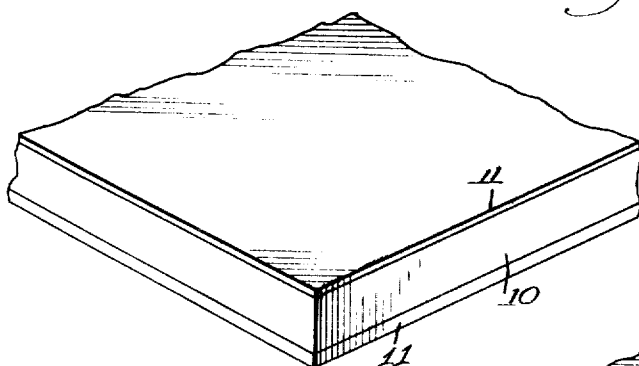


Fig. 2

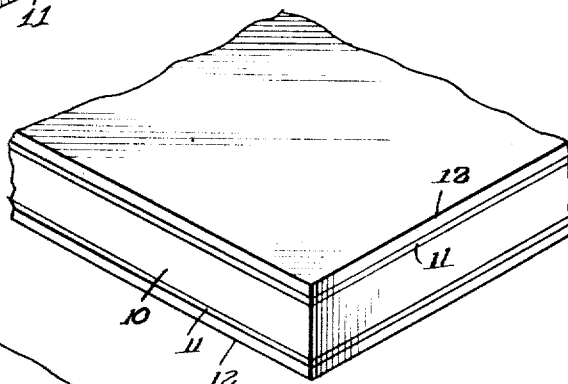


Fig. 3

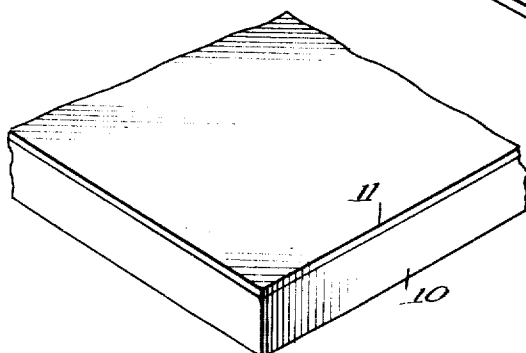
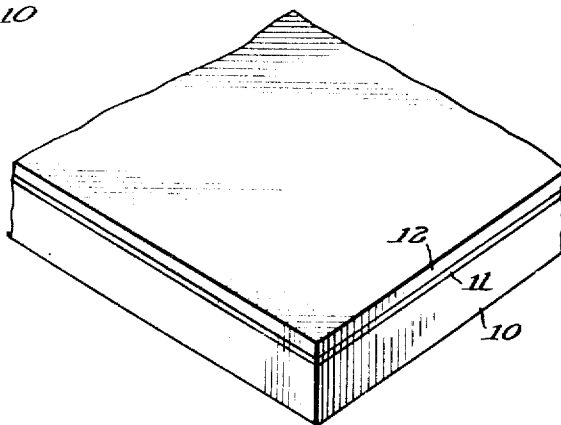


Fig. 4



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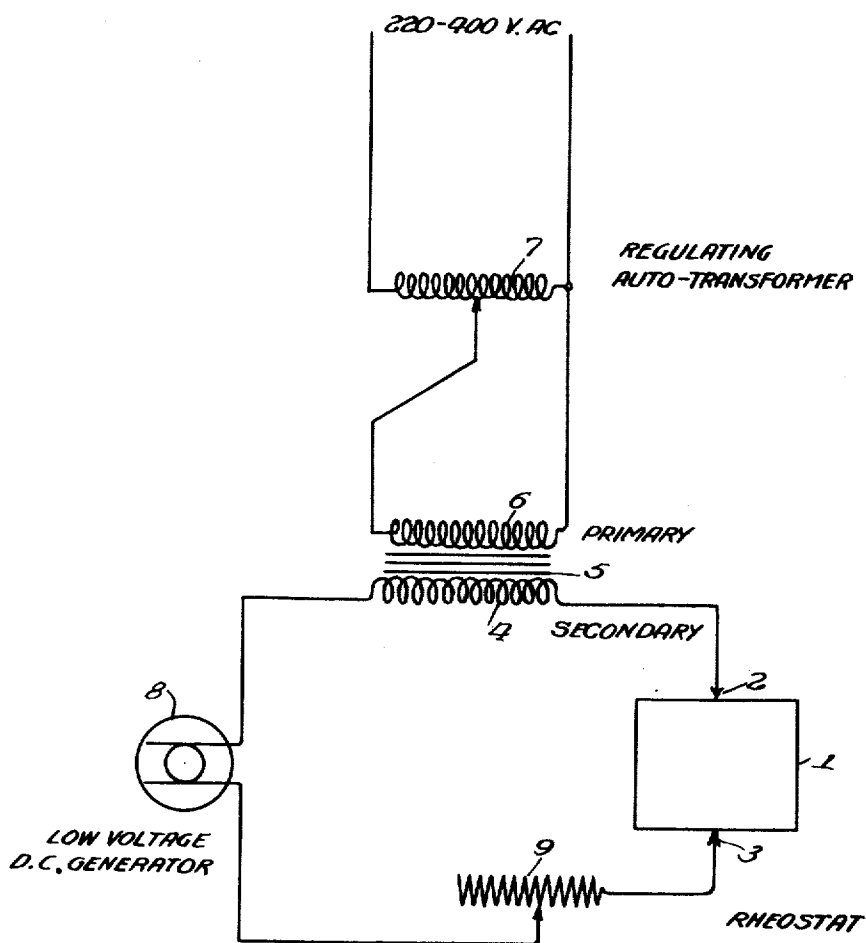
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VITREOUS ENAMELING OF FERROUS METAL

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2 Sheets-Sheet 2

Fig. 5



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UNITED STATES PATENT OFFICE

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VITREOUS ENAMELING OF FERROUS METAL

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This invention relates to vitreous enameling, more particularly to new and improved base stock for vitreous enamels, and to a new and improved method of controlling the adherence of vitreous enamels to ferrous metals.

As is well known, one of the principal problems in the art of vitreous enameling is to secure proper adherence between the vitreous enamel coating and the base stock, to which the enamel is applied, without the use of a "ground" or grip coat containing cobalt, maganese and usually nickel. It has long been recognized that it would be desirable to employ as the enamel base stock, ordinary carbon steels containing the usual percentage of carbon (e. g., 0.10% to 0.20%), but such steels are characterized by rather poor warping properties as compared with the special enamel irons or enamel steels when exposed to heat during the burning operation. As a result, the most satisfactory vitreous enamel base stocks have been specially prepared very low carbon steels (containing, say, 0.01% to 0.02% carbon) which are more expensive than many of the ordinary steels.

One of the objects of this invention is to provide a new and improved method of controlling the adherence of vitreous enamels to ferrous metal base stocks.

Another object of the invention is to provide a new and improved method of controlling the oxidation and reduction reactions which occur during the firing of a vitreous enamel.

A further object of the invention is to provide a new and improved type of material which is specially adapted to receive a coating of a vitreous enamel.

Still a further object of the invention is to provide a new and improved composition of matter containing thereon a coating or layer of an oxidizing agent sealed by another coating of a metal which is reducing in relation to iron upon thermal excitation.

An additional object is to prepare new and improved enamel base stocks from ordinary steels.

Other objects and advantages of the invention will appear from the following description in conjunction with the accompanying drawings, in which:

Fig. 1 represents in perspective a sheet of ferrous metal base stock with an oxidizing layer formed on opposite sides thereof in accordance with the invention;

Fig. 2 illustrates the ferrous metal base stock with an oxidizing layer and a reducing metal

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layer on opposite sides thereof, as provided in accordance with the invention;

Figs. 3 and 4 illustrate a ferrous metal base stock corresponding, respectively, to that shown in Figs. 1 and 2, but treated on one side only; and

Fig. 5 illustrates diagrammatically one type of apparatus which can be employed in the treatment of the base stock material.

Generally stated, the invention is based upon the discovery that the adherence of vitreous enamels to a ferrous metal base stock can be controlled by subjecting the base stock to a controlled treatment to form an oxidizing layer thereon and thereafter firing the vitreous enamel thereon in the presence of a metal which is reducing with respect to ferrous iron under the firing conditions.

This can be accomplished in several ways, but is preferably effected in accordance with the invention by applying an oxidizing layer to a ferrous metal base as a thin coating, and sealing said coating or layer exteriorly by another coating or layer of a metal which is reducing in relation to ferrous iron upon thermal excitation. The oxidizing agent used to form the oxidizing layer may be any oxidizing agent capable of oxidizing the reducing metal under enamel firing conditions. In other words, the oxidizing layer is oxidizing with respect to ferrous iron. The reducing metal can be any metal or alloy of metals below iron (Fe^{++}) in the electrochemical series (as listed, for example, in the Chemical Rubber Handbook, 19th edition, page 850) capable of forming a coating which is permanent for ordinary handling and usage and which does not flash off or sublime at temperatures up to vitreous enamel firing temperatures.

The vitreous enamel firing temperatures will vary, depending upon the composition of the vitreous enamel. For example, a high firing vitreous enamel may be fired at temperatures as high as 1650 degrees Fahrenheit while a low firing vitreous enamel may be fired at temperatures around 1250 degrees Fahrenheit, or below. The invention especially contemplates a vitreous enameling method which makes it possible to employ low firing vitreous enameling compositions which can be fired at much lower temperatures than heretofore considered feasible. The minimum firing temperature will naturally vary, depending upon the type of vitreous enameling composition, but vitreous enameling compositions firing at temperatures as low as 800 degrees Fahrenheit, or lower, are contemplated in accordance with the invention.

Apparently, there is a quantitative relation between the amounts of the oxidizing layer, the reducing metal, and the firing temperatures. Thus, a higher oxidation rate is obtained at the higher firing temperatures and a smaller amount of oxidizing layer is required to obtain optimum adherence. On the other hand, at the lower firing temperatures, a larger amount of the oxidizing layer is required to obtain optimum adherence. The invention is not limited to the use of any particular type of oxidizing layer, but good results have been obtained in practice by applying to the ferrous base stock a coating of nascently formed colloidal sulphur, such as is precipitated by adding an aqueous solution of sodium polysulphide, potassium polysulphide or other polysulphides to an aqueous sulphuric acid solution containing from 6% to 10 % of H_2SO_4 by weight. However, other oxidizing agents or materials, either elemental or in the form of compounds, organic or inorganic, which are capable of forming a deposit, layer or coating oxidizing with respect to ferrous iron on the ferrous base metal material, can be employed in accordance with the invention. Examples of such substances are selenium, manganese dioxide and oxidizing chlorides, chlorates, nitrates and/or organic oxidizing agents, such as, for example, quinones.

The invention will be further illustrated but is not limited by the following example:

Example

A cold rolled sheet metal base stock consisting of S. A. E. 1020 carbon steel was placed in an acid pickling bath for a period of three to twelve minutes.

The acid pickling bath was an aqueous bath containing 8% by weight of sulphuric acid, 1% of lactic acid, and 1 ounce per gallon of sodium acid fluoride ($NaHF_2$) heated at a temperature of 140 degrees to 150 degrees Fahrenheit.

The pickled sheet was then rinsed and put into a sodium polysulphide solution. The sodium polysulphide solution was made by dissolving 12.5 pounds of sodium sulphide (Na_2S) in 4.5 gallons of warm water together with 4.25 pounds of elemental sulphur, and refluxing for two and one-half hours at 228 degrees Fahrenheit. This bath was then allowed to cool and the pickled metal sheet was placed therein at room temperature (75 degrees Fahrenheit).

The metal sheet was then connected to one pole of alternating current transformer having a potential of 6 volts (R. M. S.) and the other pole was connected to a graphite electrode. The sheet was subjected to a current having a density of 80 amperes per square foot for one minute, thereby forming a sheet having an oxidizing layer thereon which was oxidizing in relation to ferrous iron, as illustrated in Fig. 1. Alternatively, both legs of the transformer can be connected to graphite electrodes and the sheet suspended between the electrodes in the polysulphide solution.

If desired, a wetting agent can be added to the polysulphide bath to increase the rate of drainage after the sheet has been taken from the bath. Any suitable wetting agent can be employed, such as, for example, 1% by weight of lauryl sulphate, or a correspondingly effective amount of some other high alcohol sulphate or long chain sulphate or sulphonate containing 8 to 18 carbon atoms.

The metal sheet turned a brownish black

color during the deposition of the sulphur, and the latter was probably entrained in a light hydrated and spongy iron oxide layer on the surface of the metal. When the sheet was taken out of the bath, it was spray-rinsed with water, then immersion-rinsed, and thereafter was made a cathode in a nickel-cobalt plating bath having the following composition. It is my belief that iron salts, mainly ferrous sulphate, are entrained in the pickle pits formed by the attack of the acid on the ferrous metal surface and that they are not completely removed by the rinsing operations, that these iron salts are hydrolyzed upon immersion in the sulphide bath and that colloidal sulphur is precipitated and a certain amount of iron sulphide is formed.

Grams per liter of bath	Bath Components
240	$NiSO_4 \cdot 7H_2O$
45	$NiCl_2 \cdot 6H_2O$
5	$CoCl_2 \cdot 6H_2O$
45	Boric Acid

the remaining being water.

This bath contained a metal ratio of 69.8 grams of nickel and 1.15 grams of cobalt per liter of solution. The pH of the bath was approximately 3.9. The boric acid was employed as a buffer.

The sulphur coated metal sheet was plated with an electrical hook-up of the type shown in Fig. 5 in which the plating bath was contained in a receptacle provided with one or more electrodes, generally illustrated at 2, and the sulphur coated metal sheet formed the cathode, as represented by the numeral 3.

The anode 2 was connected by suitable conductors to the secondary 4 of a power transformer having a core 5 and a primary 6. The primary 6 was connected to a regulating autotransformer, generally illustrated at 7, which in turn was connected to a suitable source of electrical energy, such as a 220 volt or 440 volt, 60 cycle, alternating current. Direct current was applied by means of a low voltage current generator, generally shown at 8, one side of which passed to the workpiece 3 through a rheostat 9, and the other side of which was connected to the secondary 4, in the manner shown. The ratio of alternating (R. M. S.) current to direct current was maintained within the range of 1:1 to 2:1, and the sheet was plated at a current density of 20 amperes per square foot as measured on a direct current ammeter for one minute. It was then taken out of the bath, rinsed, and dried. The resultant sheet comprises the base metal stock 10 containing on opposite sides thereof a layer or deposit of sulphur (oxidizing agent) and an outer layer or deposit of a reducing metal, which in this case is an alloy of nickel and cobalt containing approximately 98% nickel and 2% cobalt. The oxidizing layers are illustrated in Figs. 1 and 2 by the numeral 11 and the layers of reducing metal by the numeral 12. If the enamel coating is to be applied to only one side of the base metal sheet, the other side can be shielded during the application of the oxidizing layer and the reducing metal layers to produce sheets of the type illustrated in Figs. 3 and 4. Whether or not this is desirable will depend to some extent upon the intended use of the final product. In most cases, the vitreous enamel coating will be applied to both sides of the sheet. The time required for formation of an effective

oxidizing layer is shortened by using higher current densities and lengthened when lower current densities are used. As previously indicated, the time of the treatment (and, hence, the amount of the deposit formed) can be decreased somewhat when the vitreous enamel is a higher firing enamel. The amount of the oxidizing layer required for effectiveness in increasing adherence may also vary, depending upon the type of reducing metal employed, and will decrease generally the farther the reducing metal is removed from iron (Fe^{++}) in the electrochemical series. The effective amounts of oxidizing layer and reducing metal layer can readily be determined for any particular oxidizing layer and any particular reducing metal layer utilizing the fundamental principles outlined herein.

It will be understood that the invention is not limited to any special method for forming the oxidizing layer or the reducing metal layer on the base metal stock. The reducing metal layer can be formed by thermal vaporization of the reducing metal, by electroplating, or in any other suitable manner. Likewise, it will be understood that the method of electroplating given in the foregoing example is merely illustrative and represents a preferred way of practicing the invention. In general, the use of alternating current is more effective than other methods of depositing the oxidizing layer, and the effect is quantitative with time and current. Instead of using alternating current, direct current can be used with a reversing switch, or direct current alone may be used.

The frequency of the current may be varied and good results may be obtained, for example, with 25 cycle, 50 cycle and 60 cycle current in the deposition of the oxidizing layer (e. g., sulphur) and in the production of the abnormal wave forms preferably employed for plating the reducing metal.

A typical vitreous enamel which can be applied to a ferrous metal base stock of the type illustrated in Fig. 2 is prepared as follows:

A frit is made from the following ingredients:

	Parts by weight
Feldspar	20.9
Borax	40.2
Silica	22.9
Soda ash	5.1
Sodium nitrate	4.8
Fluor-spar	6.1

This material is mixed, smelted, fritted and dried in the usual manner, and the following mill additions are made:

Frit	(parts by weight) ..	100
Clay	(parts by frit weight) ..	7
Zirconium silicate opacifier	do ..	3
Sodium nitrite	do ..	1/4
Water	do ..	40

This material is ground or milled to a fineness of 0-25% residue on a 200 mesh screen, preferably 4-8% residue. The resultant composition is then applied as a bisque coating to the reducing metal surface of the ferrous metal stock (Fig. 1 or Fig. 2), prepared as described in the example, dried and fired at a temperature below 1580 degrees Fahrenheit, e. g., in a range of 1260 degrees Fahrenheit to 1580 degrees Fahrenheit.

When the vitreous enamel composition contains a metal which is reducing with respect to ferrous iron, e. g., antimony, arsenic, cobalt, nickel or alloys thereof, or a compound which

liberates such a reducing metal under the firing conditions, the enamel composition may be applied directly to an oxidized layer of the ferrous base metal of the type illustrated in Figs. 3 and 4, which contains no coating of reducing metal.

An important advantage of the invention lies in the fact that good adherence is obtained between vitreous enamels and ordinary or medium carbon steels, e. g., those containing 0.10% to 0.20% carbon. Steels of this type are widely used in making automobile bodies and for many other purposes where a very low carbon steel would be too expensive or lacks the necessary physical characteristics.

Having thus described the invention, what I claim and desire to secure by Letters Patent of the United States, is:

1. A method of controlling the adherence of vitreous enamels to ferrous metals which consists essentially in forming an oxidizing layer comprising essentially sulphur on a ferrous metal base stock, completely covering said oxidizing layer with a thin coating of a nickel-cobalt alloy, and firing a vitreous enamel on said nickel cobalt layer.

2. A method of controlling the adherence of vitreous enamels to ferrous metals which consists essentially in depositing a layer of sulphur on a ferrous metal base stock, sealing said layer with an electroplated layer of an alloy of nickel and cobalt containing principally nickel, applying a coating of a vitreous enamel over said alloy coating, and firing said enamel.

3. A vitreous enamel base stock consisting essentially of a ferrous metal containing a thin surface layer of colloidal sulphur and iron sulphide sealed exteriorly with a thin plated coating of a predominantly nickel alloy of nickel and cobalt which is reducing in relation to iron and does not flash off upon thermal excitation.

4. A method of controlling the adherence of vitreous enamels to ferrous metals which consists essentially in acid pickling said ferrous metal, depositing on the pickled surface colloidal sulphur, sealing said deposited sulphur with a thin coating of a plated metal from the group consisting of cobalt, nickel and alloys of cobalt with nickel, and firing a vitreous enamel on said sealing coating.

5. A method of controlling the adherence of vitreous enamels to carbon steels which consists essentially in acid pickling a steel having an average carbon content in excess of 0.02% but not more than 0.20%, depositing elemental sulphur as a coating on the pickled steel, sealing said coating of deposited sulphur with a thin coating of nickel, and firing a vitreous enamel on said sealing coating.

6. A method of controlling the adherence of vitreous enamels to carbon steels which consists essentially in acid pickling a steel having an average carbon content in excess of 0.02% but not more than 0.20%, depositing elemental sulphur as a coating on the pickled steel, sealing said coating of deposited sulphur with a thin coating of an alloy of nickel and cobalt containing principally nickel, and firing a vitreous enamel on said sealing coating.

7. In a method of preparing ferrous metals for vitreous enameling, the steps which consist essentially in acid pickling a steel having an average carbon content in excess of 0.02% but not more than 0.20%, depositing a coating of colloidal sulphur on the pickled surface of said steel, and sealing said coating with a thin plated coating of a

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metal from the group consisting of cobalt, nickel and alloys of cobalt with nickel.

8. In a method of preparing ferrous metals for vitreous enameling, the steps which consist essentially in acid pickling a steel having an average carbon content in excess of 0.02% but not more than 0.20%, depositing a coating of colloidal sulphur on the pickled surface of said steel, and sealing said coating with a thin plated coating of an alloy of nickel and cobalt containing principally nickel.

9. A vitreous enamel base stock consisting essentially of an acid pickled steel having an average carbon content in excess of 0.02% and not more than 0.20% and having thereon a coating of colloidal sulphur, said coating being completely coated and sealed with a coating of a thin plate of an alloy of nickel and cobalt which is predominantly nickel.

10. A vitreous enamel base stock consisting essentially of an acid pickled steel having an average carbon content in excess of 0.02% and not more than 0.20%, and having on the pickled surface thereof a coating of colloidal sulphur, said coating being completely coated and sealed with a coating of a thin plate of a metal from the group consisting of cobalt, nickel and alloys of cobalt with nickel.

11. A vitreous enamel coated article obtained by firing a vitreous enamel on a steel having an average carbon content in excess of 0.02% and not more than 0.20%, which has been acid pickled and has had a coating of colloidal sulphur deposited on the pickled surface and completely coated and sealed with a coating of a thin plate

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of a metal from the group consisting of cobalt, nickel and alloys of cobalt with sulphur prior to firing the vitreous enamel thereon.

12. A vitreous enamelled article obtained by firing a vitreous enamel on a steel having an average carbon content in excess of 0.02% and not more than 0.20% which has been acid pickled and has had a coating of sulphur deposited on the acid pickled surface and sealed with a thin plate of an alloy of nickel and cobalt which is predominantly nickel prior to firing the vitreous enamel thereon.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
533,945	Cochran	Feb. 12, 1895
971,641	Rice et al.	Oct. 4, 1910
1,211,218	Parker	Jan. 2, 1917
1,818,579	Pfleiderer	Aug. 11, 1931
1,819,816	Hommel	Aug. 18, 1931
1,887,967	Tanner et al.	Nov. 15, 1932
2,101,950	McGohan	Dec. 14, 1937
2,132,438	Romig	Oct. 11, 1938
2,398,881	Brown et al.	Apr. 23, 1946

FOREIGN PATENTS

Number	Country	Date
739 (of 1882)	Great Britain	Feb. 15, 1882
358,886	Great Britain	Oct. 8, 1931